⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: 0 292 317 B1

⑫ EUROPEAN PATENT SPECIFICATION

㊺ Date of publication of patent specification: 03.07.91 Bulletin 91/27

(51) Int. Cl.^{5}: C09D 163/00, C09D 163/02, C08G 59/14

㉑ Application number: 88304601.3

㉒ Date of filing: 20.05.88

(54) Film-forming resin compositions and their use for coating metals.

㉚ Priority: 22.05.87 GB 8712121

㊸ Date of publication of application:
23.11.88 Bulletin 88/47

㊺ Publication of the grant of the patent:
03.07.91 Bulletin 91/27

(84) Designated Contracting States:
AT BE CH DE ES FR GB IT LI NL SE

(56) References cited:
FR-A- 1 597 521
US-A- 2 849 418
US-A- 4 059 550
US-A- 4 452 929

(73) Proprietor: THE DOW CHEMICAL COMPANY
2030 Dow Center Abbott Road P.O. Box 1967
Midland Michigan 48640-1967 (US)

(72) Inventor: Rickett, Clive J.
Tillmatten 15
W-7580 Bühl-Eisental (DE)

(74) Representative: Raynor, John et al
W.H. Beck, Greener & Co 7 Stone Buildings
Lincoln's Inn
London WC2A 3SZ (GB)

EP 0 292 317 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Jouve, 18, rue Saint-Denis, 75001 PARIS

Description

This invention relates to film-forming resin compositions, a method for preparing them and their use for coating substrates, preferably metallic substrates.

GB-A-2 107 321 discloses a heat-curable water-dispersible film-forming resin composition which is the reaction product of a water-insoluble phenolic resin with an epoxy resin and a phosphoric acid.

This composition can be used alone or mixed with a water-dispersible epoxy resin for producing coating compositions. When the resin composition is mixed with a water-dispersible epoxy resin, the phenolic to total epoxy resin ratio is at least 1 : 5, preferably at least 1 : 3.

Furthermore, US patent 4,059,550 discloses an aqueous dispersion of a heat curable coating composition which is made from a mixture of (I) a complex polyhydroxy polyether resin which is for example terminated with epoxy groups and (II) a phenolplast resin whereby as a catalyst for the curing reaction an adduct of phosphoric acid and a glycidyl polyether of a polyhydric phenol is used.

However, formulations based on such compositions, to achieve sufficient chemical resistance for their use in food contact applications, contain an amount of phenolplast resin which renders the final coating yellow or gold in colour.

Accordingly, coating compositions disclosed in GB-A-2,107,321 and US-A-4,059,550 are not suited for applications where a stable, clear or white pigmented coating system is desirable.

EP-A-0,002,718 discloses a heat curable coating composition comprising an epoxy resin and a trimellitic anhydride-glycol ester. Such a composition gives colourless coatings suitable for white pigmentation and limited use in sanitary container applications. However, formulations based on such compositions tend to be unstable with respect to viscosity versus time due to the inherent reactivity of the anhydride species and are limited in their application due to the resulting chemical resistance properties of the cured coating.

Accordingly, it remains desirable to provide a film-forming resin composition which is useful for producing clear or white pigmented coatings which are suitable for sanitary applications.

SUMMARY OF THE INVENTION

Accordingly, one aspect of the present invention is a film-forming resin composition comprising

(A) from 3 to 7 weight percent of a phenolic resin,

(B) from 35 to 75 weight percent of an epoxy resin and

(C) from 22 to 62 weight percent of a reaction product between an epoxy resin and a phosphoric or phosphonic acid, based on the total weight of (A), (B) and (C).

Another aspect of the present invention is a method of preparing this resin composition by preparing a blend of the components (A), (B) and (C).

Still another aspect of the present invention is the use of this resin composition for coating substrates, preferably metallic substrates.

Still another aspect of the present invention is a substrate, preferably a metallic substrate, being at least partially coated with a coating prepared from this resin composition.

The film-forming resin composition of the present invention shows excellent viscosity stability over a period of time. It is very useful for preparing thermosetting coatings for metallic substrates. The cross-linked resin composition gives essentially colourless coatings of high toughness, flexibility, adhesion and chemical resistance making its use especially suited for the lining of containers for sanitary applications such as containers for food or beverages or cosmetics such as tooth pastes.

DETAILED DESCRIPTION OF THE INVENTION

The film-forming resin composition of the present invention comprises from 3, preferably from 4 weight percent, and up to 7, preferably up to 6 weight percent of a phenolic resin (A).

Suitable phenolic resins are for example reaction products of monohydric or polyhydric phenols with an aldehyde. Typical examples are resins prepared from phenol, resorcinol, o-, m- or p-cresol, xylenol, para-tertiary-butyl phenol, nitrophenol or 2,2-bis(4-hydroxyphenol) propane condensed with formaldehyde, acetaldehyde or propionaldehyde.

Preferred phenolic resins are polyalkylol phenols wherein the phenolic functionality has been at least partially etherified with e.g. methyl, ethyl or butyl groups.

Illustrative examples of phenolic resins useful herein are described in "Encyclopedia of Polymer Science and Technology", Volume 10, pages 1-68, Interscience Publishers (1969) which is hereby incorporated by reference.

The phenolic resin is preferably solid or semi-solid at ambient temperature.

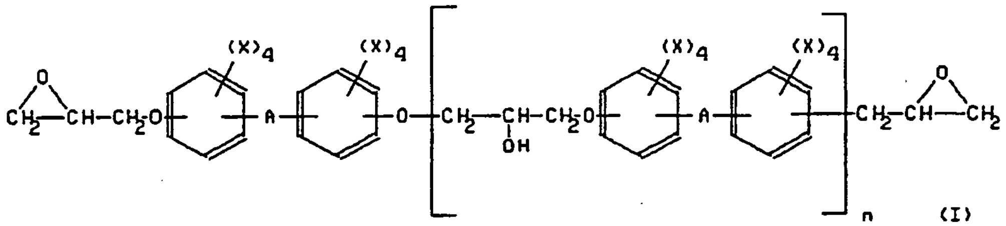
Preferred phenolic resins are those commercially available from Hoechst AG as PHENODUR PR 401, PR 515, PR 612, PR 722 or from General Electric as METHYLON 75108, or from Reichhold as VARCUM 29-170.

The film-forming resin composition of the present invention further comprises from 35, preferably from 53 weight percent, and up to 75, preferably up to 61 weight percent of an epoxy resin (B).

The epoxy resin should preferably contain on the average at least 1, most preferably from 1 to 4 epoxide groups, per molecule.

Illustrative examples of epoxy resins useful herein are described in The Handbook of Epoxy Resins by H. Lee and K. Neville, published in 1967 by McGraw-Hill, New York, in appendix 4-1, pages 4-56 and U.S. Patent Nos. 2,633,458 ; 3,477,990 (particularly column 2, line 39 to column 4, line 75) ; 3,821,243 ; 3,970,719 ; 3,975,397 and 4,071,477 and G.B. Patent Specification No. 1,597,610, all of which are incorporated herein by reference.

Epoxy resins of particular interest in the practice of the present invention include diglycidyl ethers of bisphenol compounds, particularly those compounds represented by the following general structural formula :



(I)

wherein :

each A is independently a divalent hydrocarbon group having from 1 to 6 carbon atoms, preferably methylene or isopropylidene, or a covalent bond ;

each X is independently hydrogen, an alkyl group of 1 to 6 carbon atoms or halogen, preferably chlorine or bromine ; and

n has an average value of from 0 to 50, preferably from 5 to 25, most preferably from 10 to 18.

The epoxy resin (B) is preferably solid or semi-solid at ambient temperature prior to curing.

The average epoxy equivalent weight is preferably from 172, more preferably from 1200, and preferably up to 20000, more preferably up to 5000.

The epoxy equivalent weight is the weight of epoxy resin (in grams) containing one equivalent of epoxy.

Particularly preferred epoxy resins are those wherein each A is methylene or isopropylidene, each X is independently hydrogen or bromine and n is on the average from 10 to 18. Preferred examples of these resins are bisphenol A type epoxy resins having an average epoxy equivalent weight of from 1200 to 5000. Such resins are commercially available from The Dow Chemical Company as D.E.R. 667 E, D.E.R. 668 E and D.E.R. 669 E epoxy resins.

The film-forming composition of the present invention further comprises from 22, most preferably from 35 weight percent, and up to 62, preferably up to 43 weight percent reaction product (C).

The reaction products (C) between an epoxy resin and a phosphoric or phosphonic acid are known from U.S. patents 2,541,027 ; 4,164,487 ; 4,289,812 and 4,397,970.

The reaction product (C) is preferably of the type described in detail in US patents 4,397,970 and 4,164,487 prior to the addition of the neutralising amine.

The epoxy resin component of the reaction product (C) is preferably of the type described above for epoxy resin (B) of formula I but where n has an average value of from 0 to 50, preferably from 0 to 25 and most preferably from 0 to 15.

The phosphoric acid used for preparing the reaction product (C) is most conveniently in the form of commercial anhydrous orthophosphoric acid or aqueous phosphoric acid having a concentration of at least 60 percent, but condensed forms of phosphoric acid such as polyphosphoric acid or pyrophosphoric acid can be used, as can phosphoric acid semi-hydrate $2H_3PO_4 \cdot H_2O$.

The reaction product (C) between an epoxy resin and a phosphoric or phosphonic acid can be prepared as described in US patents 4,397,970 ; 4,164,487 and 4,289,812. The reaction product (C) preferably contains from 0.1 to 10, more preferably from 0.5 to 4 weight percent phosphoric acid, based on the total amount of epoxy resin and phosphoric acid.

The resin composition of the present invention can be prepared by blending the components (A), (B) and

(C). A convenient form of mixing the resin components A, B and C and rendering them suitable for coating the substrate is by dissolving them in an organic solvent. Various solvents or mixtures thereof may be employed for this purpose and may for example include glycol ethers or their acetates such as ethoxyethanol, methoxypropanol or butoxyethanol ; esters such as ethyl acetate, isopropyl acetate, butyl acetate or amyl acetate ; or ketones such as methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone. Additionally, hydrocarbons may be included such as toluene or xylene or alcohols such as butanol, such that good wetting properties and drying characteristics are achieved for the intended substrate, coating technology and curing method.

The resin composition preferably comprises one or more of the above-mentioned solvents. The total weight of the sum of phenolic resin (A), epoxy resin (B) and reaction product (C) is preferably from 20 to 50 percent, more preferably from 30 to 40 percent, based on the total weight of the sum of (A), (B) and (C) and the solvent(s).

The resin composition of the present invention is very useful for providing unpigmented clear coatings which do not have a yellowish appearance.

The resin composition of the present invention is also very useful for providing pigmented coatings without the yellowing normally caused by the presence of a phenolic resin. For example, pigmentation with titanium dioxide will result in bright white coatings with excellent chemical resistance. The pigmented resin composition preferably comprises one or more of the above-mentioned solvents. The total weight of the sum of phenolic resin (A), epoxy resin (B) and reaction product (C) is preferably from 10 to 40 percent, more preferably from 20 to 30 percent, based on the total weight of the sum of (A), (B) and (C), the pigment(s) and the solvent(s).

The weight of the pigment(s) is preferably from 10 to 30 percent, more preferably from 15 to 25 percent, based on the total weight of the sum of (A), (B) and (C), the pigment(s) and the solvent(s).

The resin composition of the present invention can also contain known additives, for example agents for promoting cross-linking or improving the flow of the resin composition.

The coating composition can be applied to substrates such as glass, plastics or metals, preferably metals such as low tinned steel, chromed steel, black plate or aluminium, either as sheets or continuous coils by methods such as roller coating, spray coating, dip coating or curtain coating. Preformed shapes may also be coated, for example food or beverage cans by spray, dip or rinse coating techniques.

Curing or cross linking of the resin composition is preferably effected by heating the coated substrate in an air circulated oven to between 100°C and 300°C, more preferably between 180°C and 225°C for between 30 seconds and 30 minutes, more preferably 6 to 15 minutes. Alternatively, this operation may be conducted by induction heating of the coated substrate or by its exposure to infra-red radiation.

The present invention is further illustrated by the following examples which do not limit the scope of the invention. Unless otherwise specified, all parts and percentages are by weight.

The following components are used for preparing the film-forming composition of the present invention :

- Phenolic resin (A) : a phenolic resin which is commercially available from Hoechst AG under the trademark PHENODUR PR 401,
- epoxy resin (B) : a reaction product of epichlorohydrin and bisphenol-A which is commercially available from The Dow Chemical Company under the trademark D.E.R. 668 E,
- reaction product (C) between an epoxy resin and phosphoric acid (hereafter called : epoxy phosphate ester) : the epoxy phosphate ester prepared as described below,
- solvent mixture (D) : a mixture of methoxypropanol, xylene and n-butanol in a weight ratio of 2 : 2 : 1.

Epoxy phosphate ester (C) preparation

To a 10 kg steel reactor equipped with oil heating, stirrer and reflux condenser, 4131 g of D.E.R. 330 (trademark) epoxy resin is charged, together with 2068 g of bisphenol-A. The mixture is stirred and heated to 90°C and when homogenous, 600 ppm of ethyltriphenylphosphonium acetate is added. Heating is continued until an exotherm occurs at 145°C.

The temperature is held at 165°C for 60 minutes after which time 1317 g of butoxyethanol is charged and mixed at 135°C for 30 minutes until a solution is formed. Next, 310 g of a 25% solution of polyphosphoric acid in DOWANOL EB (trademark) glycol ether is added and stirred for an additional 60 minutes. Phosphorylation is complete when the epoxy content is reacted down to less than 0.1%.

2870 g of methoxypropanol is added after approximately 60 minutes and the mixture is stirred at 130°C for a further 30 minutes.

Hydrolysis of the di- and tri-ester is effected by the addition of 100.4 g of demineralised water and maintaining the reaction at 130°C for a final 150 minutes after which time the produced epoxy phosphate ester is cooled and analysed.

The product has a non-volatile content of 60 percent, based on the total weight of epoxy phosphate ester and solvent.

Example 1

Clear Lacquer Formulation

22.80 parts by weight (pbw) of the epoxy phosphate ester (C) is mixed with 20.52 pbw of the epoxy resin (B) in 54.11 pbw of the solvent blend (D). To this mixture 2.57 pbw of the phenolic resin (A) is added with stirring and left for 12 hours at room temperature.
The formulation has a non-volatile content of 36% and a Brookfield viscosity of 320 mPa · s.
The weight ratio of epoxy phosphate ester (C) : epoxy resin (B) : phenolic resin (A) is 38 : 57 : 5.

Lacquer Properties

Coatings are made on E2 tinned steel from Rasselstein AG and then cured in an air-circulated oven at 200°C for various times.

The cured film undergoes the following tests :
I. Solvent resistance : the coated plate is rubbed with an acetone soaked cotton pad until the film coating is affected. The number of double rubs is counted.
II. Flexibility ("wedge bend") : measured as described in Verpackungs-Rundschau 25 (1974), Nr. 6, Tech.-wiss. Beilage, pages 47 and 48.
III. Cross-hatch adhesion : measured according to DIN 53 151.
IV. Adhesion/flexibility ("Erichsen square cup") : Erichsen square cups of 40 mm × 40 mm are drawn on an Erichsen cupping machine model 142 and the adhesion/flexibility of the coating is tested.
The best appearance is rated as 1, the worst one as 8.
V. Acid resistance : Erichsen square cup appearance after boiling for 60 minutes in a 2% tartaric acid solution at 120°C. Rated 1-8 as above.

Cure time (min at 200°C)	8'	10'	12'	20'
Dry coating thickness (micrometers)	4.2	4.7	4.6	5.0
Solvent Resistance	30	40	45	50
Wedge Bend (%)	76	78	77	77
Cross-hatch Adhesion (%)	100	100	100	100
Erichsen Square cup	1	1	1	1
Acid Resistance	2	3	3	4

Example 2

Pigmented lacquer formulation

A millbase (predispersion) is prepared by dispersing 60.6 of pbw titanium dioxide in 10.1 pbw of the epoxy phosphate ester (C) solution described above and diluting this mixture with 29.3 pbw of the above mentioned solvent blend (D).

A formulation is made by dissolving 14.3 pbw of epoxy resin (B) in 38.4 pbw of said solvent blend (D), then mixing in 33 pbw of the above described millbase, 1.8 pbw of phenolic resin (A) and an additional 12.5 pbw of the epoxy phosphate ester (C) solution described above.

The resulting formulation has a non-volatile content of 45% and a pigment : (epoxy phosphate ester (A) + epoxy resin (B) + phenolic resin (C)) ratio of 0.8 : 1. The weight ratio of epoxy phosphate ester (C) : epoxy resin (B) : phenolic resin (A) is 38 : 57 : 5.

Formulation Stability

The stability of the pigmented lacquer formulation of Example 2 is demonstrated by monitoring the change in viscosity with time over a three month period at 40°C.

Viscosity after X weeks at 40°C (mPa.s at 25°C)

X weeks	0	3	6	9	12
Viscosity (mPa.s	240	240	240	250	260 at 25°C)

Lacquer properties

Coatings are made and tested according to the procedures in Example 1.

Cure time (min at 200°C)	8'	10'	12'	20'
Dry coating thickness micrometers)	6.6	6.5	6.2	6.9
Solvent Resistance	10	14	17	30
Wedge bend (%)	65	64	65	63
Cross-hatch adhesion (%)	100	100	100	100
Erichsen Square cup	1	1-2	1-2	2
Acid Resistance	2	2	2-3	3

Example 3

The significance of the ratio between epoxy phosphate ester (C) and epoxy resin (B) is illustrated below. A number of formulations are prepared with various ratios of the two components (C) and (B), keeping constant the amount of phenolic resin (A) (5 pbw) and curing conditions (10 min at 200°C).

Epoxy resin (B): Epoxy phosphate ester (C) (pbw)	95:0 I (comparative)	76:19 II	65:30 III	57:38 IV	38:57 V	19:76 VI	0:95 VII (comparative)
Solvent Resistance	3	5	5	14	20	20	100
Wedge bend %	42	56	61	64	70	63	60
Erichsen Square cup	1 Y	1	1	1-2	1-2	1-2	1-2
Acid Resistance	1-2 B	1-2 SB	2	2	3	4-5 SB	6 SB

where Y implies that a coating has a definite yellow tint with a Gardner colour of approximately 2.

B and SB imply (slight) blushing of the coating indicating a loss of acid resistance.

Sufficient phosphoric acid is added to the formulations I, II, IV and VI to make the total amount of free and reacted phosphoric acid in each, the same as that reacted in formulation VII.

The effect of varying the phenolic resin (A) content for the given weight ratio between epoxy resin (B) and epoxy phosphate ester (C) of 57 pbw : 38 pbw is illustrated below :

Phenolic resin content (pbw)	3	5	7
Solvent Resistance	4	14	15
Wedge bend %	62	64	66
Erichsen Square cup	1-2	1-2	1-2
Acid Resistance	2 SB	2	3-4

Claims

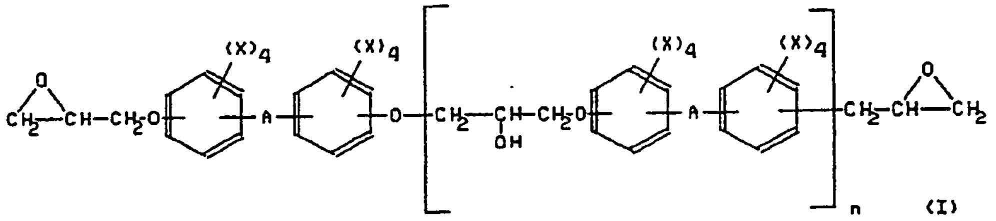
Claims for the Contracting States : AT, BE, CH, DE, FR, GB, IT, LI, NL, SE

1. A resin composition comprising
(A) from 3 to 7 weight percent of a phenolic resin,
(B) from 35 to 75 weight percent of an epoxy resin and
(C) from 22 to 62 weight percent of a reaction product between an epoxy resin and a phosphoric or phosphonic acid,
the said parts by weight being based on the total weight of (A), (B) and (C).

2. A resin composition as claimed in Claim 1, which also comprises an organic solvent.

3. The resin composition of Claim 1 or Claim 2 comprising
from 4 to 6 weight percent phenolic resin (A),
from 53 to 61 weight percent epoxy resin (B) and
from 35 to 43 weight percent reaction product (C).

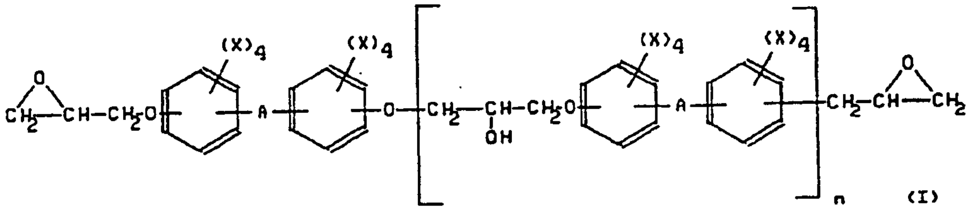
4. The resin composition of any of Claims 1 to 3 wherein the epoxy resin (B) is a resin of formula I



(I)

wherein
each A independently is a divalent hydrocarbon group having from 1 to 6 carbon atoms or a covalent bond ;
each X independently is hydrogen, an alkyl group of 1 to 6 carbon atoms or halogen and ;
n has an average value of from 0 to 50 and
wherein the reaction product (C) is the reaction product between said epoxy resin and a condensed form of phosphoric acid.

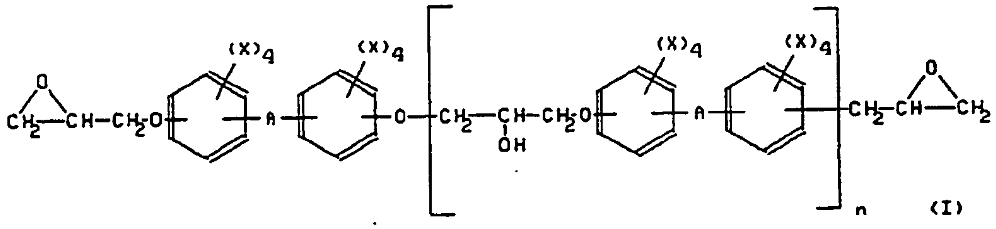
5. The resin composition of any of claims 1 to 4 wherein the epoxy resin (B) is a resin of formula I



(I)

wherein each A is isopropylidene, each X is hydrogen and n has an average value of from 5 to 25.

6. The resin composition of any of claims 1 to 5 wherein the reaction product (C) is the reaction product between an epoxy resin of formula I



(I)

wherein each A is isopropylidene, each X is hydrogen and n has an average value of from 0 to 15 and a condensed form of prosphoric acid.

7. The resin composition of any of claims 1 to 6 comprising additionally a pigment and a solvent or solvent mixture in such an amount that the total weight of the sum of phenolic resin (A), epoxy resin (B) and the reaction product (C) is from 10 to 40 percent and the weight of the pigment is from 10 to 30 percent, based on the total weight of the sum of (A), (B) and (C), the pigment and solvent (mixture).

8. Use of the resin composition of any of Claims 1 to 7 for coating substrates.

9. The use of Claim 8 for coating metallic substrates.

10. A substrate, preferably a metallic substrate, being at least partially coated with a coating prepared from the resin composition of any of Claims 1 to 7.

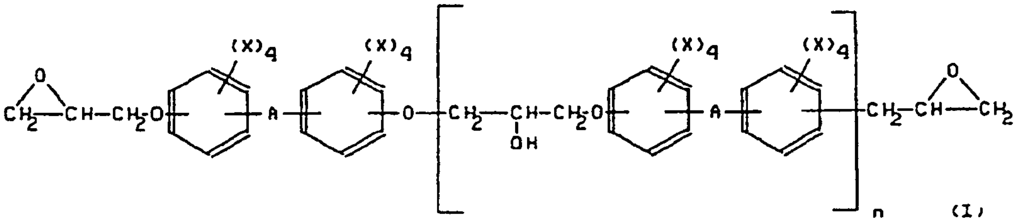
Claims for the Contracting State : ES

1. A substrate being at least partially coated with a coating prepared from a resin composition comprising
(A) from 3 to 7 weight percent of a phenolic resin,
(B) from 35 to 75 weight percent of an epoxy resin and
(C) from 22 to 62 weight percent of a reaction product between an epoxy resin and a phosphoric or phosphonic acid,
based on the total weight of (A), (B) and (C).

2. The substrate of Claim 1 wherein the resin composition from which the coating is prepared comprises an organic solvent.

3. The substrate of Claim 1 being at least partially coated with a coating prepared from the resin composition comprising
from 4 to 6 weight percent phenolic resin (A),
from 53 to 61 weight percent epoxy resin (B) and
from 35 to 43 weight percent reaction product (C).

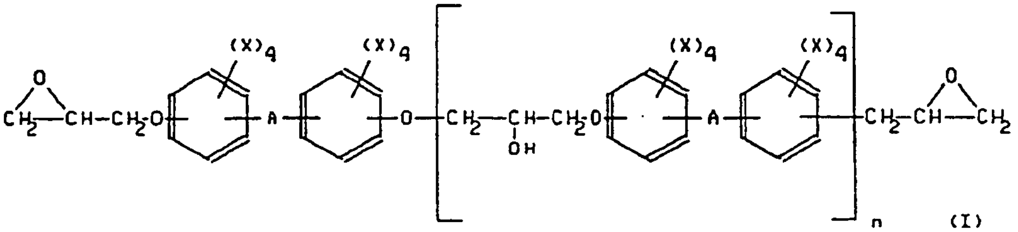
4. The substrate of any of Claims 1 to 3 being at least partially coated with a coating prepared from the resin composition wherein the epoxy resin (B) is a resin of formula I



(I)

wherein
each A independently is a divalent hydrocarbon group having from 1 to 6 carbon atoms or a covalent bond ;
each X independently is hydrogen, an alkyl group of 1 to 6 carbon atoms or halogen and ;
n has an average value of from 0 to 50 and
wherein the reaction product (C) is the reaction product between said epoxy resin and a condensed form of phosphoric acid.

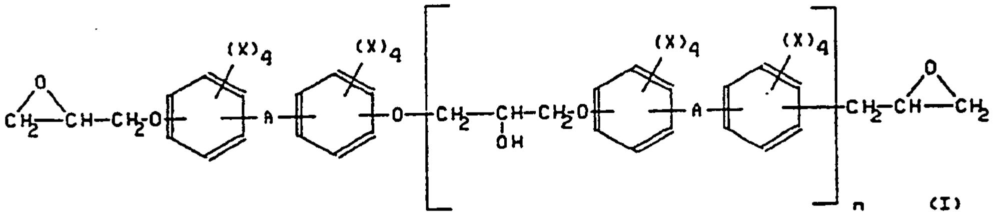
5. The substrate of any of Claims 1 to 4 being at least partially coated with a coating prepared from the resin composition wherein the epoxy resin (B) is a resin of formula I



(I)

wherein each A is isopropylidene, each X is hydrogen and n has an average value of from 5 to 25.

6. The substrate of any of Claims 1 to 5 being at least partially coated with a coating prepared from the resin composition wherein the reaction product (C) is the reaction product between an epoxy resin of formula I



(I)

wherein each A is isopropylidene, each X is hydrogen and n has an average value of from 0 to 15 and a condensed form of phosphoric acid.

7. The substrate of any of claims 1 to 6 being at least partially coated with a coating prepared from the resin composition which additionally comprises a pigment and a solvent or solvent mixture in such an amount that the total weight of the sum of phenolic resin (A), epoxy resin (B) and reaction product (C) is from 10 to 40 percent and the weight of the pigment is from 10 to 30 percent, based on the total weight of the sum of (A), (B) and (C), the pigment and solvent (mixture).

8. The substrate of any of claims 1 to 7 being metallic.

9. A method of preparing the coated substrate of any of claims 1 to 8 wherein the resin composition is applied to the uncoated substrate and cured on the substrate.

10. The method of claim 9 wherein the resin composition is cured at a temperature between 100°C and 300°C for a period of 30 seconds to 30 minutes.

Ansprüche

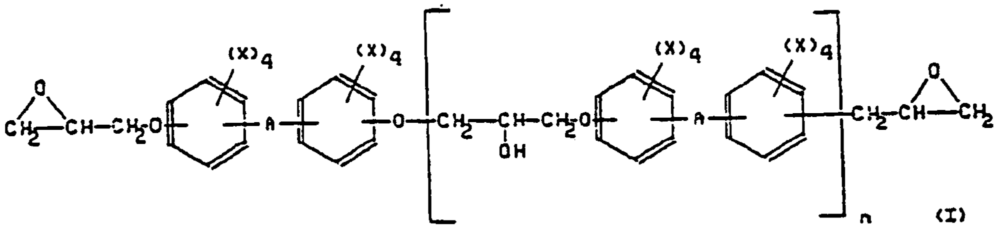
Patentansprüche für die Vertragsstaaten : AT, BE, CH, DE, FR, GB, IT, LI, NL, SE

1. Harzzusammensetzung enthaltend
(A) von 3 bis 7 Gew.-% eines Phenolharzes,
(B) von 35 bis 75 Gew.-% eines Epoxyharzes und
(C) von 22 bis 62 Gew.-% eines Reaktionsproduktes eines Epoxyharzes und einer Phosphorsäure oder Phosphonsäure,
wobei sich die Gewichtsprozente auf Gesamtgewicht von (A), (B) und C) beziehen.

2. Harzzusammensetzung nach Anspruch 1, **dadurch gekennzeichnet**, daß sie auch ein organisches Lösemittel enthält.

3. Harzzusammensetzung nach Anspruch 1 oder Anspruch 2, **dadurch gekennzeichnet**, daß sie von 4 bis 6 Gew.-% Phenolharz (A), von 53 bis 61 Gew.-% Epoxyharz (B) und von 35 bis 43 Gew.-% Reaktionsprodukt (C) enthält.

4. Harzzusammensetzung nach jedem der Ansprüche 1 bis 3, **dadurch gekennzeichnet**, daß das Epoxyharz (B) ein Harz der Formel I ist

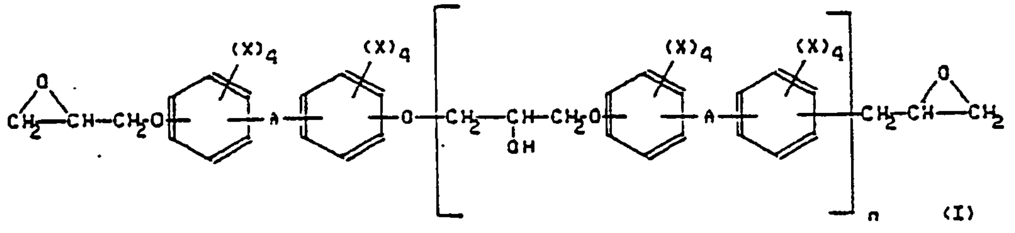


(I)

in der jedes A unabhängig eine zweiwertige Kohlenwasserstoffgruppe mit 1 bis 6 Kohlenstoffatomen oder eine

kovalente Bindung ist, jedes X ist unabhängig Wasserstoff, eine Alkylgruppe mit 1 bis 6 Kohlenstoffatomen oder Halogen und n hat einen Mittelwert von 0 bis 50 und wobei das Reaktionsprodukt (C) das Reaktionsprodukt von dem Epoxyharz und einer kondensierten Form von Phosphorsäure ist.

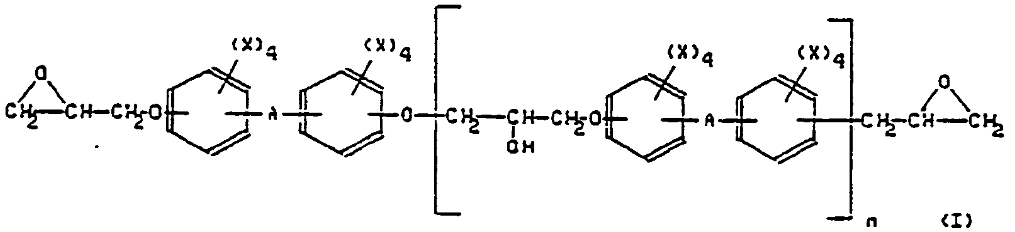
5. Harzzusammensetzung nach jedem der Ansprüche 1 bis 4, **dadurch gekennzeichnet**, daß das Epoxyharz (B) ein Harz der Formel I ist



(I)

in der jedes A Isopropyliden ist, jedes X Wasserstoff ist und n einen Mittelwert von 5 bis 25 hat.

6. Harzzusammensetzung nach jedem der Ansprüche 1 bis 5, **dadurch gekennzeichnet**, daß das Reaktionsprodukt (C) das Reaktionsprodukt eines Epoxyharzes der Formel I ist



(I)

in der jedes A Isopropyliden ist, jedes X Wasserstoff ist und n einen Mittelwert von 0 bis 15 hat, und einer kondensierten Form von Phosphorsäure ist.

7. Harzzusammensetzung nach jedem der Ansprüche 1 bis 6, **dadurch gekennzeichnet**, daß sie zusätzlich ein Pigment und ein Lösemittel oder Lösemittelgemisch in einer solchen Menge enthält, daß das Gesamtgewicht der Summe von Phenolharz (A), Epoxyharz (B) und Reaktionsprodukt (C) von 10 bis 40 Prozent und das Gewicht des Pigmentes von 10 bis 30 Prozent, bezogen auf Gesamtgewicht der Summe von (A), (B) und (C), dem Pigment und Lösemittel (gemisch) beträgt.

8. Verwendung der Harzzusammensetzung nach jedem der Ansprüche 1 bis 7 zum Beschichten von Trägern.

9. Verwendung nach Anspruch 8 zum Beschichten von Metallträgern.

10. Träger, vorzugsweise metallischer Träger, zumindest teilweise beschichtet mit einer Beschichtung, hergestellt aus der Harzzusammensetzung nach jedem der Ansprüche 1 bis 7.

Patentansprüche für den Vertragsstaat : ES

1. Träger, mindestens teilweise beschichtet mit einer Beschichtung, hergestellt aus einer Harzzusammensetzung, enthaltend

(A) von 3 bis 7 Gew.-% eines Phenolharzes,
(B) von 35 bis 75 Gew.-% eines Epoxyharzes und
(C) von 22 bis 62 Gew.-% eines Reaktionsproduktes eines Epoxyharzes und einer Phosphorsäure oder Phosphonsäure,

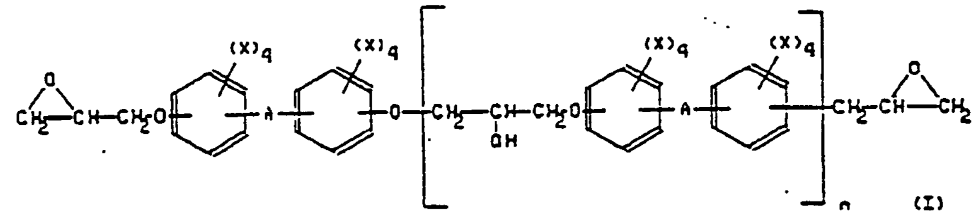
wobei sich die Gewichtsprozente auf Gesamtgewicht von (A), (B) und C) beziehen.

2. Träger nach Anspruch 1, **dadurch gekennzeichnet**, daß die Harzzusammensetzung, aus der die Beschichtung hergestellt ist, ein organisches Lösemittel enthält.

3. Träger nach Anspruch 1, **dadurch gekennzeichnet**, daß er mindestens teilweise mit einer Beschichtung versehen ist, die hergestellt ist aus einer Harzzusammensetzung enthaltend von 4 bis 6 Gew.-% Phenolharz (A), von 53 bis 61 Gew.-% Epoxyharz (B) und von 35 bis 43 Gew.-% Reaktionsprodukt (C).

4. Träger nach jedem der Ansprüche 1 bis 3, **dadurch gekennzeichnet**, daß er mindestens teilweise mit

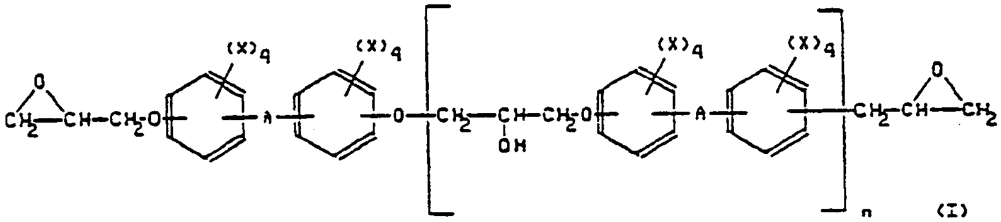
einer Beschichtung versehen ist, hergestellt aus der Harzzusammensetzung, in der das Epoxyharz (B) ein Harz der Formel I ist



(I)

in der jedes A unabhängig eine zweiwertige Kohlenwasserstoffgruppe mit 1 bis 6 Kohlenstoffatomen oder eine kovalente Bindung ist, jedes X ist unabhängig Wasserstoff, eine Alkylgruppe mit 1 bis 6 Kohlenstoffatomen oder Halogen ist und n einen Mittelwert von 0 bis 50 hat und wobei das Reaktionsprodukt (C) das Reaktionsprodukt von dem Epoxyharz und einer kondensierten Form von Phosphorsäure ist.

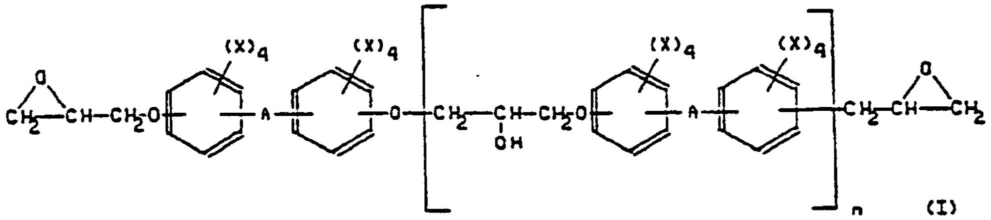
5. Träger nach jedem der Ansprüche 1 bis 4, **dadurch gekennzeichnet**, daß er mindestens teilweise mit einer Beschichtung versehen ist, hergestellt aus der Harzzusammensetzung, in der das Epoxyharz (B) ein Harz der Formel I ist



(I)

in der jedes A Isopropyliden-ist, jedes X Wasserstoff ist und n einen Mittelwert von 5 bis 25 hat.

6. Träger nach jedem der Ansprüche 1 bis 5, **dadurch gekennzeichnet**, daß er zumindest teilweise mit einer Beschichtung versehen ist, hergestellt aus der Harzzusammensetzung, in der das Reaktionsprodukt (C) das Reaktionsprodukt eines Epoxyharzes der Formel I ist



(I)

in der jedes A Isopropyliden ist, jedes X Wasserstoff ist und n einen Mittelwert von 0 bis 15 hat, und einer kondensierten Form von Phosphorsäure ist.

7. Träger nach jedem der Ansprüche 1 bis 6, **dadurch gekennzeichnet**, daß er zumindest teilweise mit einer Beschichtung versehen ist, hergestellt aus der Harzzusammensetzung, die zusätzlich ein Pigment und ein Lösemittel oder Lösemittelgemisch in einer solchen Menge enthält, daß das Gesamtgewicht der Summe von Phenolharz (A), Epoxyharz (B) und Reaktionsprodukt (C) von 10 bis 40 Prozent und das Gewicht des Pigmentes von 10 bis 30 Prozent, bezogen auf Gesamtgewicht der Summe von (A), (B) und (C), dem Pigment und Lösemittel (gemisch) beträgt.

8. Träger nach jedem der Ansprüche 1 bis 7, **dadurch gekennzeichnet**, daß er metallisch ist.

9. Verfahren zum Herstellen eines beschichteten Trägers nach jedem der Ansprüche 1 bis 8, **dadurch gekennzeichnet**, daß die Harzzusammensetzung auf den unbeschichteten Träger aufgebracht und auf dem Träger gehärtet wird.

10. Verfahren nach Anspruch 9, **dadurch gekennzeichnet**, daß die Harzzusammensetzung bei einer Temperatur zwischen 100°C und 300°C während 30 Sekunden bis 30 Minuten gehärtet wird.

Revendications

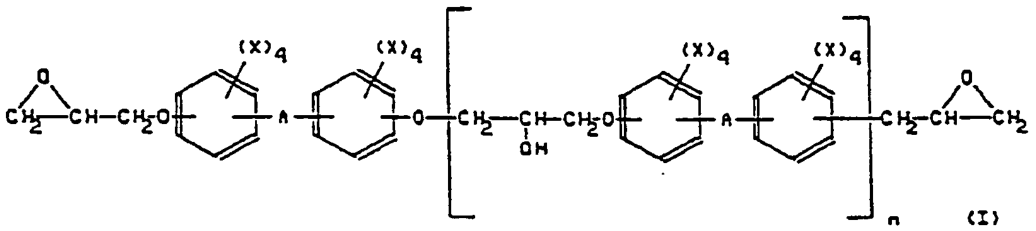
Revendications pour les Etats contractants : AT, BE, CH, DE, FR, GB, IT, LI, NL, SE

1. Composition de résine qui comprend
(A) de 3 à 7 pour-cent en poids d'une résine phénolique,
(B) de 35 à 75 pour-cent en poids d'une résine époxy et
(C) de 22 à 62 pour-cent en poids d'un produit de réaction entre une résine époxy et un acide phosphorique ou phosphonique,
lesdites parties en poids étant données par rapport au poids total de (A), (B) et (C).

2. Composition de résine selon la revendication 1, qui comprend également un solvant organique.

3. Composition de résine selon la revendication 1 ou 2, qui comprend
de 4 à 6 pour-cent en poids d'une résine phénolique (A),
de 53 à 61 pour-cent en poids d'une résine époxy (B), et
de 35 à 43 pour-cent en poids du produit de réaction (C).

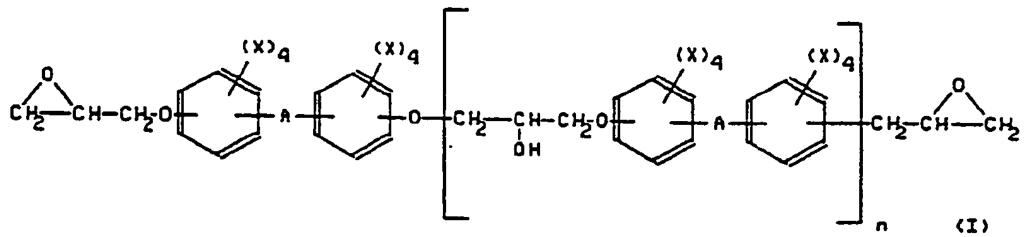
4. Composition de résine selon l'une quelconque des revendications 1 à 3, dans laquelle la résine époxy (B) est une résine de formule (I)



(I)

dans laquelle chaque A représente de manière indépendante un groupe hydrocarboné divalent ayant de 1 à 6 atomes de carbone ou une liaison covalente ; chaque X représente de manière indépendante un atome d'hydrogène, un groupe alkyle avec de 1 à 6 atomes de carbone ou un atome d'halogène et n possède une valeur moyenne de 0 à 50, et dans laquelle le produit de réaction (C) est le produit de réaction entre ladite résine époxy et une forme condensée d'acide phosphorique.

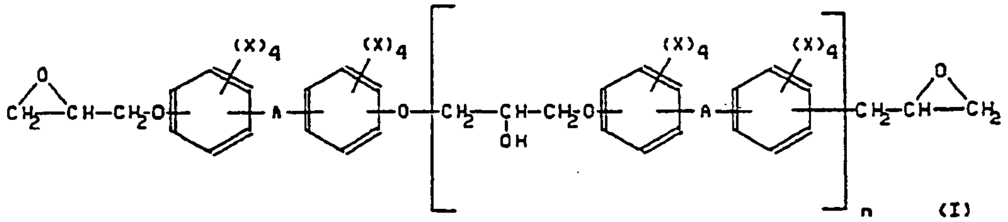
5. Composition de résine selon l'une quelconque des revendications 1 à 4, dans laquelle la résine époxy (B) est une résine de formule (I)



(I)

dans laquelle chaque A représente l'isopropylidène, chaque X représente un atome d'hydrogène et n possède une valeur moyenne de 5 à 25.

6. Composition de résine selon l'une quelconque des revendications 1 à 5, dans laquelle le produit de réaction (C) est le produit de réaction entre une résine époxy de formule (I)



(I)

dans laquelle chaque A représente l'isopropylidène, chaque X représente un atome d'hydrogène et n possède une valeur moyenne de 0 à 15 et une forme condensée d'acide phosphorique.

7. Composition de résine selon l'une quelconque des revendications 1 à 6, qui comprend en outre un pigment et un solvant ou un mélange de solvants en une quantité telle que le poids total de la somme de la résine phénolique (A), de la résine époxy (B) et du produit de réaction (C) est compris entre 10 et 40 pour-cent et le poids du pigment est compris entre 10 et 30 pour-cent, par rapport au poids total de la somme de (A), (B) et (C), du pigment et du solvant (mélange).

8. Utilisation de la composition de résine selon l'une quelconque des revendications 1 à 7, pour recouvrir des substrats.

9. Utilisation selon la revendication 8, pour recouvrir des substrats métalliques.

10. Substrat, de préférence un substrat métallique, qui est au moins partiellement recouvert d'un revêtement préparé à partir de la composistion de résine selon l'une quelconque des revendications 1 à 7.

Revendications Pour l'Etat contractant : ES

1. Substrat qui est au moins partiellement recouvert d'un revêtement préparé à partir d'une composition de résine qui comprend

(A) de 3 à 7 pour-cent en poids d'une résine phénolique,

(B) de 35 à 75 pour-cent en poids d'une résine époxy et

(C) de 22 à 62 pour-cent en poids d'un produit de réaction entre une résine époxy et un acide phosphorique ou phosphonique,

par rapport au poids total de (A), (B) et (C).

2. Substrat selon la revendication 1, dans lequel la composition de résine à partir de laquelle on prépare le revêtement comprend un solvant organique.

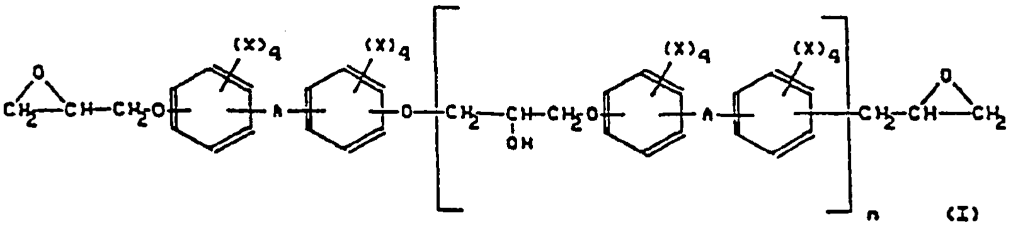
3. Substrat selon la revendication 1, qui est au moins partiellement recouvert d'un revêtement préparé à partir de la composition de résine qui comprend

de 4 à 6 pour-cent en poids d'une résine phénolique (A),

de 53 à 61 pour-cent en poids d'une résine époxy (B), et

de 35 à 43 pour-cent en poids du produit de réaction (C).

4. Substrat selon l'une quelconque des revendications 1 à 3, qui est au moins partiellement recouvert d'un revêtement préparé à partir de la composition de résine dans laquelle la résine époxy (B) est une résine de formule (I)

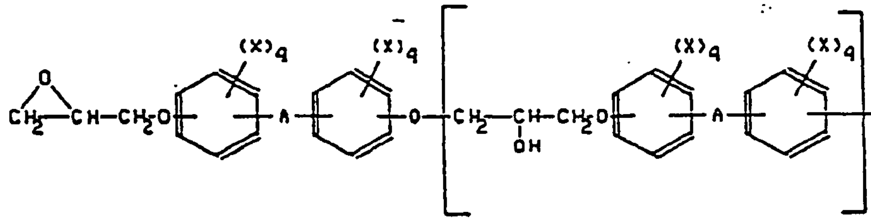


(I)

dans laquelle chaque A représente de manière indépendante un groupe hydrocarboné divalent ayant de 1 à 6 atomes de carbone ou une liaison covalente ; chaque X représente de manière indépendante un atome d'hydrogène, un groupe alkyle avec de 1 à 6 atomes de carbone ou un atome d'halogène et n possède une valeur moyenne de 0 à 50, et dans laquelle le produit de réaction (C) est le produit de réaction entre ladite résine époxy et une forme condensée d'acide phosphorique.

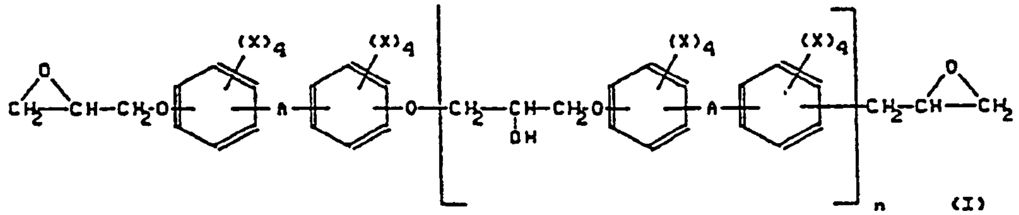
5. Substrat selon l'une quelconque des revendications 1 à 4, qui est au moins partiellement recouvert d'un

revêtement préparé à partir de la composition de résine dans laquelle la résine époxy (B) est une résine de formule (I)


(I)

dans laquelle chaque A représente l'isopropylidène, chaque X représente un atome d'hydrogène et n possède une valeur moyenne de 5 à 25.

6. Substrat selon l'une quelconque des revendications 1 à 5, qui est au moins partiellement recouvert d'un revêtement préparé à partir de la composition de résine dans laquelle le produit de réaction (C) est le produit de réaction entre une résine époxy de formule (I)


(I)

dans laquelle chaque A représente l'isopropylidène, chaque X représente un atome d'hydrogène et n posède une valeur poyenne de 0 à 15 et une forme condensée d'acide phosphorique.

7. Substrat selon l'une quelconque des revendications 1 à 6, qui est au moins partiellement recouvert d'un revêtement préparé à partir de la composition de résine qui comprend en outre un pigment et un solvant ou un mélange de solvants en une quantité telle que le poids total de la somme de la résine phénolique (A), de la résine époxy (B) et du produit de réaction (C) est compris entre 10 et 40 pour-cent et le poids du pigment est compris entre 10 et 30 pour-cent, par rapport au poids total de la somme de (A), (B) et (C), du pigment et du solvant (mélange).

8. Substrat selon l'une quelconque des revendications 1 à 7 qui est métallique.

9. Procédé de préparation du substrat recouvert selon l'une quelconque des revendications 1 à 8, dans lequel on applique la composition de résine sur le substrat non recouvert et on la fait durcir sur le substrat.

10. Procédé selon la revendication 9, dans lequel on fait durcir la composition de résine à une température comprise entre 100°C et 300°C pendant une période de 30 secondes à 30 minutes.